PATENT SPECIFICATION

957,048

957,048

Date of Application and filing Complete Specification: July 25, 1960. No. 25806/60

Application made in Italy (No. 12935) on July 30, 1959.

Complete Specification Published: May 6, 1964.

Index at Acceptance:—C1 AE1X.

International Classification:—C 01 b.

COMPLETE SPECIFICATION

NO DRAWINGS

Process for Recovering Sodium Borohydride from a Suspension thereof with Sodium Methylate in Petroleum Oil

We, MONTECATINI SOCIETA GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA, a Body Corporate organised and existing under the laws of Italy, of 18 Via Filippo Turati, Milan, Italy, do hereby declare this invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to sodium borohydride and provides an improved process for its recovery.

Sodium borohydride is generally prepared by reacting sodium hydride with trimethyl borate in suspension in a petroleum oil under atmospheric or superatmospheric pressure, and at a temperature of 250°C to 280°C.

$$4\,NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$$

The petroleum oil employed is the oil commonly known as "Vaseline" oil but any high boiling hydrocarbon oil will do. This oil has a low carbon deposition at high temperatures and is thus particularly suited for employment in the reaction. The word "Vaseline" is a registered Trade Mark.

The reaction product is a suspension of sodium borohydride and sodium methylate in the oil, from which the sodium borohydride has to be separated.

For this purpose various solvents have been proposed such as liquid ammonia and ethylene diamine, which are insoluble in the oil, or *iso*propylamine, or diethylene glycol dimethyl ether, which are soluble in it.

By employing these solvents one obtains, after filtation, separation of the phases and distillation, the separation of the three components.

The oil is recycled, the sodium methylate is decomposed with water for production of caustic soda and methanol, but the sodium borohydride produced has, after drying, a purity of only about 90%. To obtain sodium borohydride with purity higher than 96-98%, a complicated process of crystallisation of the borohydride from its aqueous solutions rendered basic by the addition of NaOH was proposed recently.

In the practice of the proposed processes various difficulties have been encountered. For example, in the case of use of ethylene diamine, emulsions are formed with the oil and sodium methylate, which can be broken only with extreme difficulty; also the process of crystallisation of sodium borohydride from aqueous solutions is difficult to carry out.

It is an object of the present invention to provide a simple advantageous and economical process for producing sodium borohydride of high purity. Another object is to provide directly sodium hydroxide and methanol as by-products.

There is provided by the present invention a method of recovering sodium borohydride from a suspension thereof with sodium methylate in petroleum oil which method comprises the steps of extracting said suspension with water separating the aqueous phase so produced containing said sodium borohydride and methanol and sodium hydroxide and removing the methanol therefrom and thereafter recovering said sodium borohydride from the resulting aqueous solution thereof with said sodium hydroxide.

The sodium methylate is decomposed by the water into caustic soda (NaOH) and methanol; whence, as a result, an aqueous-alcoholic solution of sodium hydroxide and sodium borohydride is obtained. This solution can be easily separated from the oil thanks to its high density either by simple

decantation or by centrifuging. The addition of water to the suspension and the separation of the two liquid layers is conveniently realized at room temperature, but it is also possible to employ a higher temperature, for example 20°C- or 50°C-60°C at which the separation of the two liquid layers takes place more easily (the upper temperature limit is that of decomposition of the borohydride, namely about 100°C). The phrase "room temperature" is used herein in the sense generally accepted in scientific literature to mean about 15°-25°C.

Methanol may now be recovered by fractional distillation of the mixture. This distillation may be carried out at ordinary pressure, but more conveniently under vacuum, to avoid any decomposition of the borohydride. The recovered methyl alcohol may be recycled by reacting it with boric acid to obtain trimethyl borate. Subsequently the water is evaporated to produce a dry solid residue. This evaporation may be carried out in a drying oven at atmospheric pressure, but the operation may be more conveniently carried out by concentrating the solution under vacuum until a fairly dense syrup is obtained which can be evaporated to dryness at atmospheric pressure. Of course it is also possible to distil the methanol and water completely under vacuum.

On the dry residue comprising a mixture of 80% of NaOH 80% and of 20% of $NaBH_4$ it is now possible to easily effect an extraction with a non-aqueous solvent for the borohydride, such as ethylene diamine, liquid ammonia and *iso*propyl amine. The solid substance is agitated in the presence of the solvent liquid and the suspension obtained is filtered. After proper washing of the residue with more solvent liquid, a sodium borohydride solution is obtained on the one hand and, on the other hand, a product constituted by substantially pure caustic soda. By evaporation of the solvent from the solution obtained, a solid substance is obtained as a residue, which is constituted by borohydride of high-grade purity. The solvent of course may be recovered and recycled. Other solvents for borohydride that may be used are for example dimethylformamide, n-propyl amine, n-butyl amine, or dimethyl-sulfoxide. The invention is further illustrated by the following example:

A sodium hydride suspension in Esso T.3 "Vaseline" oil (a paraffin oil, which possesses characteristics particularly suited for this specific use, that is, satisfactory resistance to high temperatures without showing carbonization phenomena) was reacted at atmospheric pressure with trimethyl borate at a temperature of 250-280°C. The reaction product contains $NaBH_4$ = 3.77%; NaH = 1.08%; $NaOCH_3$ = 16.1% and is constituted by whitish suspension of these compounds in "Vaseline" oil. To 113 g. of this suspension, 30 g of distilled water were added, and the mixture was agitated for 4 hours at room temperature. After 12 hours standing, the two layers were separated by means of a separating funnel. The aqueous alcoholic layer was subjected to fractional vacuum distillation, (residual pressure 25 mm) and 9.2 g of methyl alcohol were recovered by condensation. Distillation was continued under vacuum until 36 g of fairly dense syrup containing $NaBH_4$ = 11.8%; NaOH = 44.4%; H_2O = 40.2% were obtained. The mixture was then placed in an oven at 130°C temperature and on termination of drying 21.5 g of a solid residue containing 19.6% of $NaBH_4$ were obtained. 30g of anhydrous ethylene diamine d = 0.9031 were added to the residue. After agitating for 4 hours, the liquid was separated from the solid residue by filtration and the solid substance was washed 3 times on the filter with 5 g of ethylene diamine each time.

From the filtrate obtained the ethylene diamine was distilled off at ordinary pressure and, finally the residue was dried in an oven at 140°C until disappearance of the ethylene diamine odour. The solid obtained comprised 4.3 g of 97.5-98% sodium borohydride.

The most important advantages of this process are due to the fact that since the paraffin suspension is to be treated with water, all the operations after the discharge of the petroleum oil suspension reaction product from the autoclave can be carried out safely in the air, without any fear that atmospheric moisture absorbed might pollute the product thereby prejudicing the extraction process. Only the final extraction with ethylene diamine or with another solvent should be carried out in the absence of moisture, which however is easy to accomplish.

The process as herein described may be carried out at normal pressure and at a temperature higher than 250°C by employing suspension agents having a boiling point around that temperature, but preferably higher, namely "Vaseline" oil, or other high-boiling petroleum oils. Operation may be carried out however under pressure, without departing from the scope of the invention, in which case a much greater number of suspension media can be resorted to.

WHAT WE CLAIM IS:

1. A method of recovering sodium borohydride from a suspension thereof with sodium methylate in petroleum oil which method comprises the steps of extracting said suspension with water separating the aqueous phase so produced

containing said sodium borohydride and methanol and sodium hydroxde and removing the methanol therefrom and thereafter recovering said sodium borohydride from the resulting aqueous solution thereof with said sodium hydroxide.

2. A method according to Claim 1 wherein said aqueous phase is vacuum distilled to remove said methanol.

3. A method accordng to Claim 2 wherein the residue of said vacuum distillation is evaporated under vacuum to a syrupy consistency and thereafter under atmospheric pressure to dryness.

4. A method according to Claim 3 wherein the dry residue of said evaporation is extracted with a non-aqueous solvent for said sodium borohydride and the solution of said sodium borohydride so obtained filtered and evaporated to dryness to yield a residue of sodium borohydride.

5. A method according to Claim 4 wherein said solvent is ethylene diamine, *iso*propyl amine or liquid ammonia.

6. A method according to any of the preceding claims wherein said extraction with water is effected at a temperature of from 20° to 60°C.

7. A method of recovering sodium borohydride from a suspension thereof with sodium methylate in "Vaseline" oil substantially as hereinbefore described with reference to the Example.

8. Sodium borohydride when produced by the method of any of the preceding Claims.

ERIC POTTER & CLARKSON,
Chartered Patent Agents.
317, High Holborn,
London, W.C.1.

Berwick-upon-Tweed: Printed for Her Majesty's S tationery Office by The Tweeddale Press Ltd.—1964
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2. from which copies may be ob tained.